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Bound-Bound Ar-NO A-X Vibronic Transitions: Mass-Resolved 1+1 Resonance Enhanced Multiphoton Ionization (REMPI) Observations

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1. INTRODUCTION

Gas-phase processes, such as combustion and atmospheric chemistry, are governed by the forces which act between molecules, and these forces are conveniently represented by intermolecular potentials. Spectroscopic techniques provide the most direct information on the bound regions of such potentials, and rare gas (RG)-open-shell diatom van der Waals complexes have served as prototypes for developing relevant experimental and theoretical techniques. Moreover, open-shell van der Waals systems are interesting in their own right, possessing nonzero electronic spin and/or orbital angular momentum, which can couple with the vibrational and rotational angular momentum of the complex to produce novel perturbations in the rovibronic structure. The breadth of systems studied spectroscopically has grown dramatically in recent years (Heaven 1992), and general theoretical approaches for deriving (radially averaged) angular potential energy curves from the experimental results are beginning to mature (Chakravarty et al. 1990; Dubernet, Flower, and Hutson 1991; Chang et al. 1992; Green and Lester 1992; Dubernet, Tuckey, and Hutson 1992).

The Ar + NO system was one of the first RG-open-shell diatom systems to be studied, and a number of states have been characterized. The existence of bound Ar-NO complexes was initially established in a molecular beam deflection experiment (Novick et al. 1973). Subsequent to this work, Langridge-Smith, Carrasquillo, and Levy (1981) probed a supersonic expansion of NO doped Ar via LIF near the NO A-X (0,0) transition and observed a broad feature centered about 350 cm^{-1} above the NO A-X band origin. It was demonstrated that the spectra corresponded to a photodissociation process in which NO was formed in its A state, and the feature was attributed to Ar-NO. The first conclusive spectroscopic observation of Ar-NO was reported by Mills, Western, and Howard (1986a). These researchers resolved ground state rovibrational structure in an electric resonance experiment and analyzed the results in terms of a theoretical formalism based on a rigid model Hamiltonian (Mills, Western, and Howard 1986a; 1986b). From the analysis, it was concluded that the minimum in the ground state potential was associated with a nearly T-shaped (85°) configuration, and that the equilibrium internuclear distance was 3.71 Å. Scattering and theoretical studies of the NO (X) - Ar interaction have also been reported (Nielson, Parker, and Pack 1977; Thuis et al. 1980; Joswig, Andresen, and Schinke 1982; Cassavechia, Lagana, and Volpi 1984; Alexander 1993; Schmelz, Romus, and Alexander 1994). The recent ab initio study by Alexander and coworkers (Schmelz, Romus, and Alexander 1994) supports the conclusions derived by Mills, Western, and Howard (1986a; 1986b) and provides a template for refined characterization of this state. Information on the vibronic structure of the Ar-NO B, C, and D states has been obtained in resonance enhanced multiphoton

ionization (REMPI) studies (Sato, Achiba, and Kimura 1984; Miller and Cheng 1985). These states were found to be more strongly bound than the ground state.

The NO A state has pure Rydberg ($3s\sigma$) state character and lies only $44,000\text{ cm}^{-1}$ above the ground state, making it a convenient prototype for studying RG-open-shell diatom Rydberg states. Despite the advances that have been made for other Ar-NO states, details of the Ar-NO potential associated with the NO $A^2\Sigma^+$ state have remained in question. Miller (1989) reported the first evidence that the Ar-NO A state had a potential minimum, observing a structured spectrum at the 70-amu (Ar-NO^+) mass channel in a 1+1 REMPI study. The spacing between the observed features was typically $10 \pm 3\text{ cm}^{-1}$, and it was postulated that the features might be a bending progression in the Ar-NO complex. However, space charge effects precluded a characterization of the spectrum near the NO band origin, and the possibility that some of the features were associated with higher order clusters could not be ruled out. Thus no attempt was made to vibrationally assign the features. Sato et al. (1986) probed the potential in a range $200\text{--}500\text{ cm}^{-1}$ above the dissociation limit and observed an "anomalous" rotational state distribution of the NO A state photoproducts. This distribution was attributed to a rotational rainbow effect, similar to that observed in inelastic scattering studies (Schinke and Bowman 1983). Other information on the A state has been inferred from matrix isolation (Marikawa et al. 1988) and fluorescence quenching (McDermid and Laudenslayer 1982) studies.

Employing an apparatus that avoided some of the problems which hindered Miller's experiments, we reinvestigated the mass resolved 1+1 REMPI A-X spectrum of Ar-NO. Mass resolution was provided by a time-of-flight mass spectrometer (TOFMS). The spectra obtained in the current work identifies previously unresolved bands in the high-frequency portion of the spectrum; resolves vibronic band contours (bandhead structure) in several bands; and provides information on the spectral region near the NO A-X band origin. Based on this new information, the band associated with transitions between the vibrationless X and A state levels can be assigned. This assignment provides a basis for revising the estimate of the A state dissociation limit. The assignment of transitions associated with vibrationally excited X and A state levels is also discussed. For this purpose, the A state vibrational energy levels are labeled (v, n^K, v_s) , where v is the NO A state vibrational level, n is the rotational angular momentum of the diatom, K is the projection of n on the internuclear axis, and v_s is the Ar-NO stretching frequency.

At about the same time the results of this technical report were published in the open literature (McQuaid, Lemire, and Sausa 1994), a paper by Tsuji, Shibuya, and Obi (1994) appeared that contained

bound-bound *A-X* spectra with partially resolved rotational structure. Where the publications overlap, the results and conclusions are consistent. The results obtained by Tsuji, Shibuya, and Obi (1994) also confirm details of the *A* state potential about which we could only speculate. Their results are discussed in the following sections, and where appropriate, they are used to update the analysis we presented in McQuaid, Lemire, and Sausa (1994).

2. EXPERIMENTAL CONSIDERATIONS

The molecular beam/TOFMS system used in this study has been described previously (Lemire, Simeonsson, and Sausa 1993; Simeonsson, Lemire, and Sausa 1993). The complexes were formed in a pulsed supersonic expansion of rare gas(es) doped with NO. A number of different expansion compositions were employed, with NO concentrations ranging from 0.1 to 5.0%, and Ar concentrations ranging from 10 to 100% of the balance. For Ar concentrations less than 100% of the balance, helium was employed as a diluent. All of the gases employed in this study were reported by the manufacturer to exceed 99.99% purity, and they were used as purchased. The various mixtures were expanded through an 800- μm orifice via a pulsed valve (R. M. Jordan and Associates) with backing pressures ranging from 1 to 4 atm.

The probe radiation was supplied by an excimer pumped dye laser (Lumonics, HyperEx 400/Hyper-Dye 300). The laser was operated with Coumarin 450 dye to produce frequencies in the range 22,075 to 22,200 cm^{-1} . The line width of this laser is reported to be 0.08 cm^{-1} at 18,000 cm^{-1} . The dye laser frequency was doubled into the 44,150–44,400 cm^{-1} range with a synchronously tuned BBO crystal. Probe energies were typically in the range of 100–300 $\mu\text{J}/\text{pulse}$, and the change in relative intensities across this frequency range is small. The output was focused in the ion acceleration region of the TOFMS with either a 1 or 0.5 m focal length lens. A calibrated delay between the expansion onset (pulsed valve opening) and the laser pulse was provided by a digital delay generator (Stanford Research Systems). The laser and pulsed valve were triggered at 10 Hz.

The TOFMS (R. M. Jordan and Associates) is a 1-m reflectron design with a multichannel plate ion detector. The reflecting plate voltages were set to values based on previous experience with this instrument (700 V, 1,250 V) and were not changed during the course of these experiments. The ion acceleration voltages were initially set by optimizing signal associated with an NO *A-X* transition, then making small adjustments to maximize the signal at the 70-amu channel, once one was detected.

Extraction potentials were in the range of 500–1,000 V. The detector output was displayed on a 125-MHz digital oscilloscope (LeCroy 9000), and spectra associated with selected mass channels were acquired via a boxcar integrator (Stanford Research Systems). The boxcar was interfaced with a PC for data digitization and subsequent analysis. The spectra were calibrated against NO A-X transitions. The NO A-X line positions were calculated based on rotational constants derived from Engleman and Rouse (1971) and Johns, Reid, and Lepard (1977). The absolute frequencies reported in this work are considered to be accurate to $\pm 1 \text{ cm}^{-1}$. Frequency differences are considered accurate to $\pm 0.2 \text{ cm}^{-1}$.

3. RESULTS AND DISCUSSION

Presented in Figure 1 are spectra representative of those acquired in this investigation at the 70-amu (Ar-NO⁺) TOFMS channel. No attempt has been made to correct the spectra for variation in laser pulse energy. Based on NO transitions, it is considered that the minimum spectral line width (FWHM) for a given rovibronic transition is 0.6 cm^{-1} . The halfwidths of the bandheads observed in Figure 1 are consistent with this measurement. This is much broader than the laser line width. Saturation broadening is thought to contribute to this broadening, but its relative significance is unknown. Signal-to-noise levels become a problem at lower probe energies, so no systematic attempt was made to reduce the pulse energy.

The frequencies of the observed transitions are in the same range as those observed previously by Miller (1989), and there is correspondence between his results and Figure 1. However, in the current system, the 70-amu mass channel is well separated from the 30-amu (NO⁺) channel, and simple (10 shot) averaging of the Ar-NO⁺ channel was sufficient to achieve reasonable signal-to-noise levels. (Miller reported averaging 100 shots and having to make a large baseline correction due to overflow from the NO⁺ channel.) The improved capability of the experimental apparatus employed in this study provides several new observations. First, the spectrum near the NO A-X band origin was acquired. Small artifacts associated with space-charge effects and/or loss of detector sensitivity are observed in this region, but they are not considered significant from the standpoint of characterizing the Ar-NO signature. As will be discussed next, no feature ascribable to Ar-NO was observed in this region. Second, the spectrum in the range 44,265–44,295 cm^{-1} is composed of six or more vibronic transitions, compared to the one large feature shown in Miller (1989). Finally, bandhead structure is observed for at least seven bands (A-G).

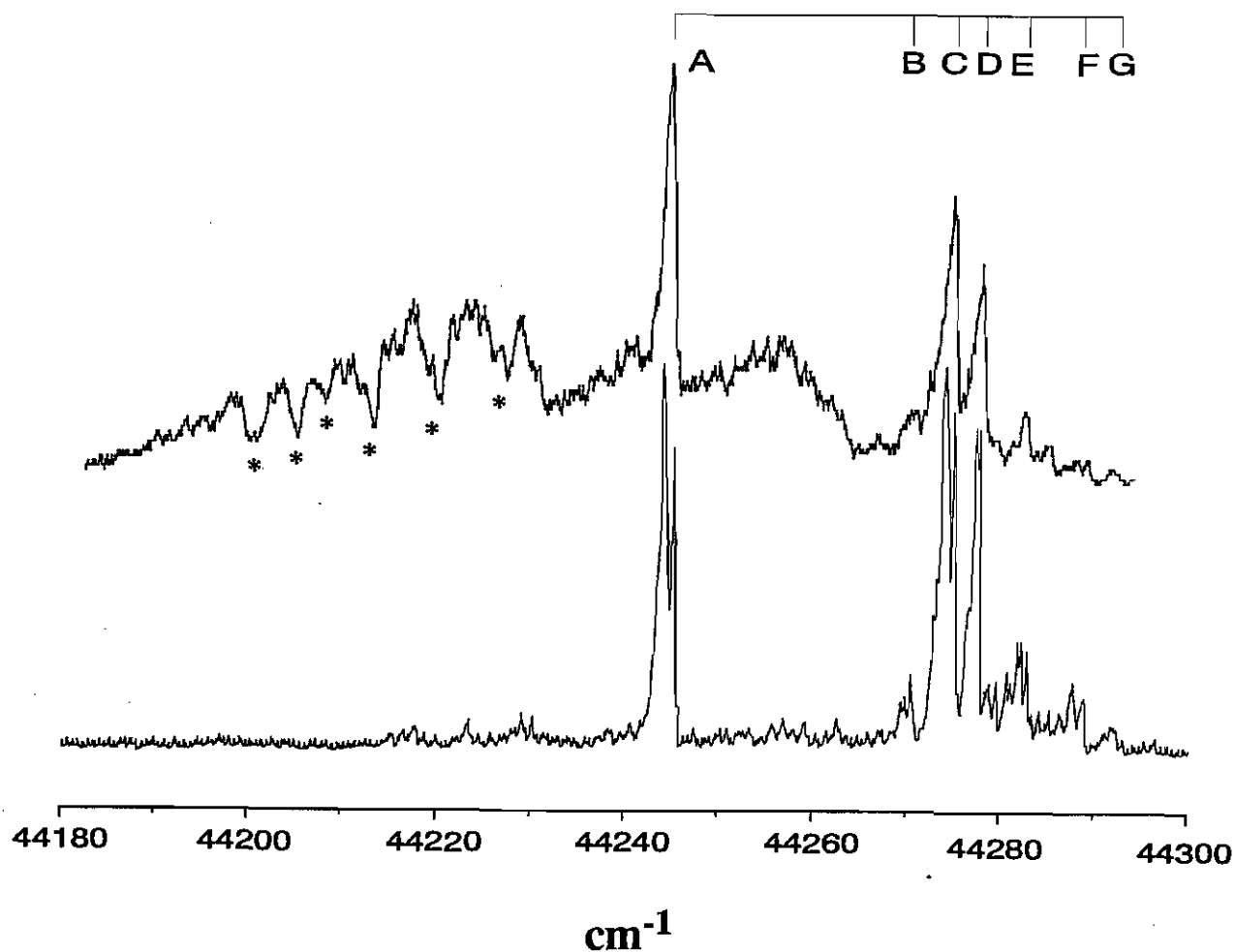


Figure 1. Representative 1+1 REMPI spectra associated with the 70-amu (Ar-NO^+) TOFMS mass channel. Features labeled with an asterisk (*) are artifacts associated with NO A-X transitions. The upper spectrum was taken at a slightly longer valve opening-laser pulse delay.

Another observation was that the spectral intensity distribution varied as a function of experimental settings. Within experimental error, the bands labeled A-G were found to have approximately the same intensity relative to each other over the range of experimental conditions employed, while the broad feature(s) in the range $44,180\text{--}44,265\text{ cm}^{-1}$ had an alternate dependence. In this regard, quantifiable differences were observed with respect to the gas pulse-laser pulse delay. It was found that the intensities

of Bands A–G peaked at shorter gas pulse-laser pulse delays than the other set of features. Based on this information, we consider that the spectra reported by Miller were carried by more than one species.

Figure 2 represents a qualitative (1-D) picture of the relation between the Ar-NO A and X potentials as understood from previous studies. In particular, the equilibrium internuclear distance in the A state is much larger than in the X state. For the given experimental parameters, it is assumed that the Ar-NO is populated exclusively in $v_s = 0$ ground state levels. Transitions from such levels will produce vibronic bands with a bandhead in the R branch and a red degraded contour. The contours of Bands A–G are consistent with this picture. These observations, coupled with the behavior of the relative intensities noted previously, are considered strong evidence that Bands A–G are associated with Ar-NO transitions. The other features are presumably associated with higher order clusters $(\text{Ar}_x(\text{NO})_y, x+y \geq 3)$ which photodissociate in the ion acceleration region to form Ar-NO^+ . (Moreover, since transitions at energies lower than the lowest energy Ar-NO transition are observed, "concerted" dissociations— $\text{Ar}_x(\text{NO})_y \rightarrow \text{Ar-NO} + \text{Ar}_{x-1}(\text{NO})_{y-1}$ —are presumably involved.) The bandhead locations of Bands A–G are listed in Table 1.

Based on the previous discussion, it is considered that Band A is the transition between vibrationless levels of the Ar-NO X and A states. (A feature at this frequency is also observed in Miller's spectrum, but it is comparable in intensity to other features and was not assigned.) This level is 43.8 cm^{-1} higher in energy than the NO A-X $Q_1(0.5)$ transition, and this difference represents the difference in dissociation energies ($D_0'' - D_0'$) of the Ar-NO X and A states. The X state dissociation energy has been characterized in spectroscopic (Sato et al. 1986; Tsuji, Shibuya, and Obi 1994), scattering (Thuis et al. 1980; Cassavechia, Lagana, and Volpi 1984), and theoretical (Joswig, Andresen, and Schinke 1982; Schmelz, Romus, and Alexander 1994) studies. These studies tend to support a D_0'' value near 90 cm^{-1} . Employing the spectroscopic characterization of this parameter ($D_0'' \leq 87 \text{ cm}^{-1}$) determined by Sato et al. (1986) yields an upper limit for the A state dissociation energy of $D_0' \leq 43 \text{ cm}^{-1}$. Tsuji, Shibuya, and Obi (1994) estimated that the A state binding from threshold excitation energy necessary to produce a specific rotational energy level of NO A state and found $D_0' = 44.3 \text{ cm}^{-1}$. (We had speculated in McQuaid, Lemire, and Sausa [1994] that the dissociation energy would be close to the upper bound obtained using Sato's data.) The upper state vibrational levels associated with Bands F–G are thus above the dissociation limit and are presumably associated with metastable dissociative levels such as those observed for the Ar-OH (A) state (Lester et al. 1993) and the Ar-CH (B) state (Alexander et al. 1994).

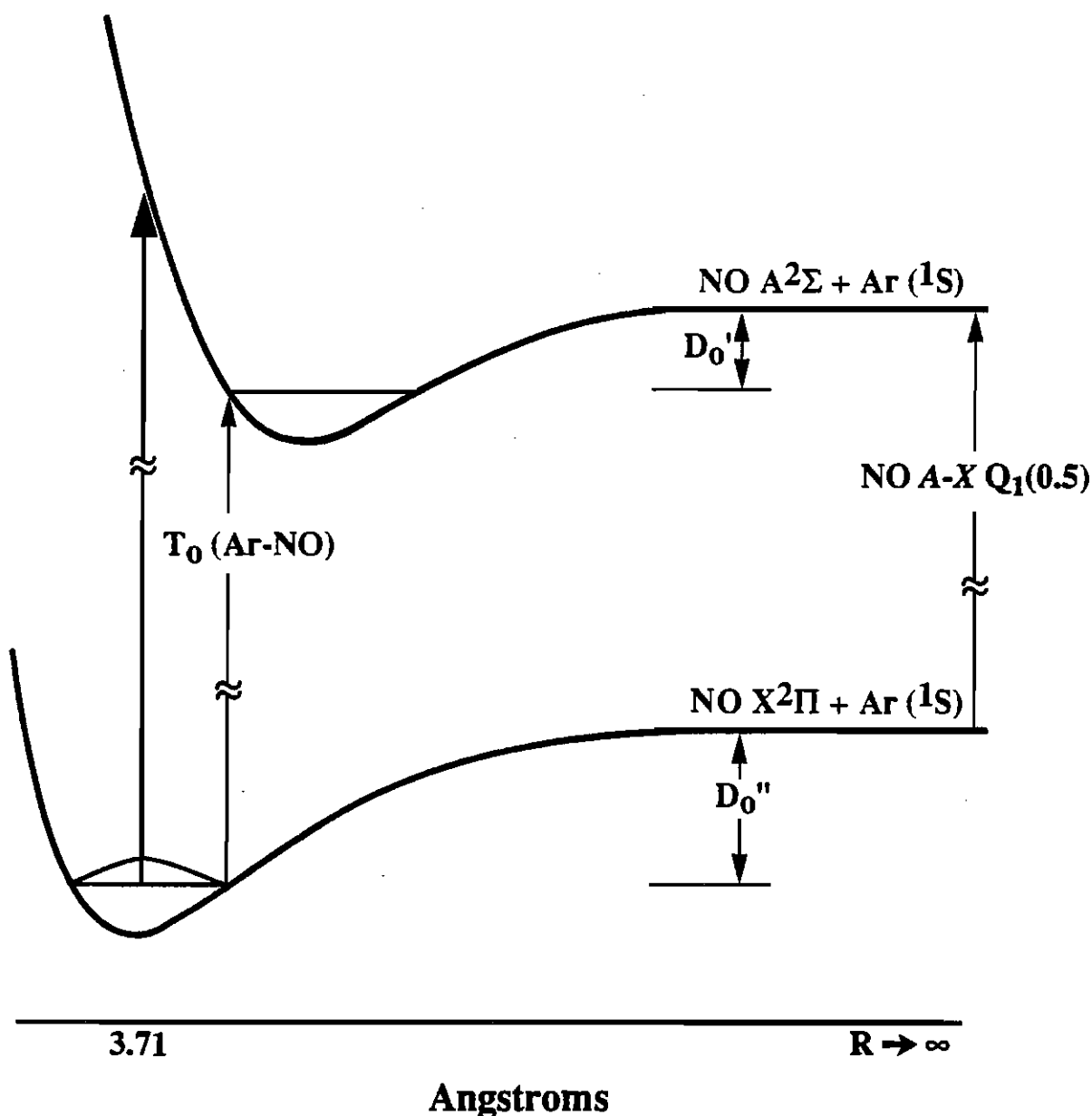


Figure 2. Qualitative representation of the relative stretching coordinate positions of the Ar-NO X and A state intermolecular potentials.

The vibrational levels involved in the transitions corresponding to Bands B–G are uncertain. Since the minimum of the ground state is centered under the repulsive wall of the A state potential, simple (1-D) Franck-Condon overlap considerations suggest that the intensity of a transition from the ground vibrational level to the $(0,0^0,1)$ level will be greater than the intensity of the transition from the ground vibrational level to the $(0,0^0,0)$ level (see Figure 2). This indicates Band C, not B, is the transition from the vibrationless ground state to the A state $(0,0^0,1)$ level. We note that Tsuji, Shibuya, and Obi (1994) do not even mention Band B, even though it is apparent in their spectra.

Table 1. Ar-NO A-X Band Positions and Proposed Assignments

Band	Proposed Assignment ^a	Bandhead Position (/cm ⁻¹)	Difference From Band A (cm ⁻¹)
NO A-X Q ₁ (0.5)		44,200.7 ^b	
A	(0,0 ⁰ ,0)	44,244.5	
B	^c	44,270.5	26.0
C	(0,0 ⁰ ,1)	44,274.4	29.9
D	(0,1 ¹ ,1)	44,277.4	32.9
E	(0,1 ⁰ ,1)	44,282.1	37.6
F		44,289.2	44.7
G		44,292.1	47.6

^a Where assignments are proposed, the transition is considered to originate from the ground vibronic level. The assignment given is for the Ar-NO A state vibronic level.

^b Line position based on Engleman and Rouse (1971) and Johns, Reid, and Lepard (1977).

^c Considered to be a transition from an excited vibrational level of the X state to the A state (0,0⁰,1) level.

The assignment of Band C as a transition to the (0,0⁰,1) level is surprising since it implies that the fundamental stretching frequency is large compared to the dissociation energy ($G(1) = 29.9 \text{ cm}^{-1}$ v. $D_0' \leq 43 \text{ cm}^{-1}$). In addressing this issue, it was considered whether the ionization step could "mask" the spectrum, permitting observation of Bands A and C but not intermediate stretching ($v_s > 0$) levels. Based on the signal-to-noise ratio in the spectra, it is considered that such a mask would have to produce at least an order of magnitude enhancement of Bands A and C compared to transitions in the 30 cm^{-1} range between them. Direct resonance in the ionization step (electron energy = 0) is perhaps the only phenomena that could produce such a significant effect. However, the energy level structure of the Ar-NO⁺ X state (Takahashi 1992) is unlikely to produce such a mask. Also, the results reported by Miller (1989) and Tsuji, Shibuya, and Obi (1994) for the complexes associated with the NO A state $v = 1$ level are nearly identical with those of the $v = 0$ level. The possibility that these two spectra are masked in the same way is considered extremely remote. Thus it is considered that there is no intermediate stretching levels between Bands A and C and that the Ar-NO A state fundamental stretching frequency is unusually large compared to the well depth. Coupled with the observed metastable states, the result strongly suggests the existence of a centrifugal barrier to dissociation. This speculation was confirmed in shape resonance experiments conducted by Tsuji, Shibuya, and Obi (1994) from which they estimate a barrier of 24 cm^{-1} .

Having concluded that Band C is the transition between the vibrationless ground level and the A state $(0,0^0,1)$ level, the energy level separations of C, D, and E were analyzed in terms of the hindered rotor formalism of Dubernet, Flower, and Hutson (1991) to address the possibility that D and E are bending levels $(0,1^K,1)$. In this approach, which neglects bend-stretch coupling, the angular potential energy $V(\theta)$ is given in terms of a Legendre polynomial expansion with radially averaged coefficients V_l ,

$$V(\theta) = \sum V_l P_l(\cos\theta), \quad (1)$$

where θ is the angle between the axis joining the Ar and NO center of masses and the diatom axis. Coefficients for two-term expansions that reproduce the energy separations of these levels were obtained by trial and error. Nominal values for two solutions are $(V_1 = 0.0 \text{ cm}^{-1}, V_2 = 8.5 \text{ cm}^{-1})$ and $(V_1 = 1.9 \text{ cm}^{-1}, V_2 = -9.5 \text{ cm}^{-1})$. (The error limits are large, and these solutions should not be construed as unique.) The former solution associates D with the $(0,1^1,1)$ level and E with the $(0,1^0,1)$ level; and corresponds to a potential with a global minimum at 90° and a barrier to hindered internal rotation of 13 cm^{-1} . The latter solution associates D with the $(0,1^0,1)$ level and E with the $(0,1^1,1)$ level. The potential has global and secondary minima at linear orientations and a barrier to hindered internal rotation of 17 cm^{-1} . While the assignments of D and E can not be determined by this analysis alone, the lack of spectroscopically observable $n = 1, v_s = 0$ A state levels and the results reported by Sato et al. (1986) favor a T-shaped potential. The assignments in Table 1 reflect these considerations. Based on the rotational constants obtained from the partially resolved rotational structure of Bands A, C, and D, Tsuji, Shibuya, and Obi (1994) concluded that C and D involved excitation of the stretching coordinate (not the bending coordinate alone), but they did not try to further assign the vibrational levels.

In the study by Sato et al. (1986), the rotational distribution of NO A state products formed via photodissociation on the Ar-NO A state repulsive wall $200\text{--}500 \text{ cm}^{-1}$ above the dissociation limit was characterized. The researchers were initially surprised to see high A state J levels populated since they expected that the Ar-NO A state orientation was similar to the ground state, and high J level production in such processes are typically associated with changes in geometry. Using a model potential, the researchers showed that such a distribution could be realized if the product distribution was controlled by the dynamics on the A state surface. The model potential was based on a Leonard-Jones (12,6) characterization with well depth ($\epsilon = 45 \text{ cm}^{-1}$) and equilibrium internuclear distance ($R_m = 4.73 \text{ \AA}$) parameters taken from the Ar-Na potential curve (Kramer and LeBreton 1967), and the anisotropy was chosen to mimic the Ar-NO X state equilibrium geometry (T-shaped). The Ar-Na potential was considered

relevant since, like the Ar-NO A state, it involves a 3s Rydberg orbital - Ar interaction. Although good agreement between the theory and the experimentally observed results were obtained, simplifications in the analysis limit the extent to which quantitative details of the A state potential are determined. Thus, the study does not give conclusive support for the K assignments given in Table 1 for Bands D and E.

The assignment of Band C as the $A(0,0^0,1) - X(0,0^0,0)$ transition leaves two possibilities for the assignment of Band B: (1) a transition from an excited bending level of the ground state to the $A(0,0^0,1)$ level, or (2) a transition from vibrationless ground state level to an $A(0,n^K,0)$ level which borrows intensity via a bend-stretch coupling with the $A(0,0^0,1)$ level. Transitions from excited bending levels of the ground state are not typically observed for the RG-open-shell systems formed in a jet expansion, but the best studied systems to date have involved diatom hydrides with large rotational constants ($B_0'' > 10 \text{ cm}^{-1}$). Since the hindered internal rotational energy levels scale with the diatom rotational energy levels (Dubernet, Flower, and Hutson 1991) and the B value of NO ($B_0'' = 1.696 \text{ cm}^{-1}$) (Johns, Reid, and Lepard 1977) is relatively small, this may not be the case. Assuming Bands B and C terminate on the same A state level, an X state bending level 3.9 cm^{-1} above the vibrationless level would be indicated. From an energy separation standpoint, this value ($\Delta E = 2.3B_0''$) is reasonable (Dubernet, Flower, and Hutson 1991). However, it follows from this conclusion that a band red-shifted 3.9 cm^{-1} from Band A should be apparent. Such a feature is observed, but low signal-to-noise levels prevent definitive correlation of it with Bands A–G. Thus, the origin of this band remains uncertain.

4. SUMMARY

New observations in the 1+1 REMPI spectrum of bound-bound Ar-NO A - X transitions have been analyzed, providing identification of the transition between vibrationless A and X state levels and a refined estimate of the A state dissociation limit ($D_0' \leq 43 \text{ cm}^{-1}$). Assignments have also been proposed (Table 1) for transitions involving vibrationally excited A state levels. These assignments assume the intensity distributions observed in the 1+1 REMPI spectra reflect (expected) Franck-Condon overlap of the X and A state levels. More work is necessary to validate the proposed assignments and establish assignments for Bands F–G. The current results should provide a useful benchmark for a detailed theoretical description of the Ar-NO A state potential.

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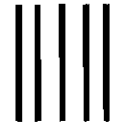
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